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THEORY OF ALPHA-RAY COUNTING FROM SOLID SOURCES¹

By N. B. KEEVIL² AND W. E. GRASHAM³

Abstract

The theory of alpha-ray counting from thin sources of atomic dimensions, from layers whose equivalent thickness is less than the range of the particle, and from thick sources is developed, assuming uniform collection over the surface such as obtained in parallel-plate collection chambers, with and without absorbers. For alpha-ray counting from rocks which normally contain 25 alpha-ray emitters, resultant equations and curves are given which can be used directly in computing actual emission from observed count. A test of the theory by experimental results on granite is given.

Introduction

With the initiation of systematic alpha-ray counting measurements at the University of Toronto, it was necessary to extend the theory of absorption of alpha-rays by solid deposits, and to test the derived equations experimentally. In this paper the theory of counting from deposits on the inner face of a parallel-plate, condenser-type chamber is developed for single alpha-ray emitters, and for mixtures emitting alpha particles of different ranges. The results are expressed in useful form by equations and convenient graphical methods. Applications to alpha-ray counting from rocks which normally contain 25 different alpha-ray emitters are discussed.

Emission from Films Approaching Atomic Dimensions

In films thin enough to possess no significant stopping power for alpha-rays, all the particles emitted towards the counting chamber can be detected, but those in the lower half of the sphere which includes all directions of emission cannot be counted in parallel-plate chambers. In this case the ratio of countable rays, c , to total number of emitted rays, α , is simply $\frac{1}{2}$; this is the maximum fraction of emitted rays which can enter the chamber. It is convenient to use the term $2c/\alpha$, defined as the *counting efficiency*. In this case, with zero absorption and uniform collection over the surface, the counting efficiency is 100%.

$$2c/\alpha = 1. \quad (1)$$

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If an absorber of thickness or stopping power x air-cm. and density ρ is placed over such a thin radioactive layer emitting N alpha-rays per sq. cm. of a surface whose area is A sq. cm., the fraction counted will be less than $\frac{1}{2}$, reaching zero when x exceeds the effective range, R' air-cm.

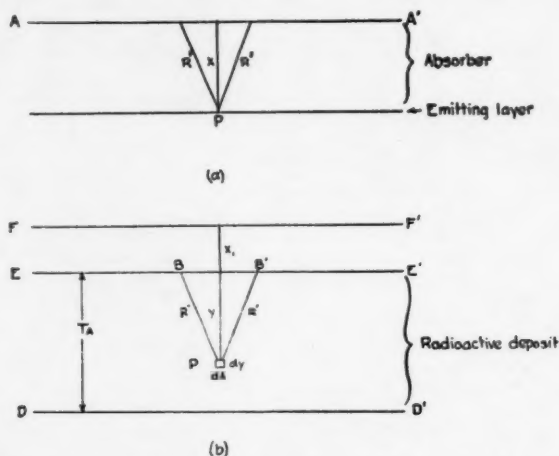


FIG. 1. Geometry for (a) an infinitely thin source and (b) a source of thickness T_A air-cm. (superimposed absorber of thickness x_1 air-cm.).

A cone with its vertex at P in the source, its base at the top of the absorber AA' , and of sloping sides R' (Fig. 1a) contains all paths of alpha particles which may be counted above the absorber. Particles taking paths outside this cone will not reach the surface with sufficient ionizing power to be detected. The number of alpha particles emitted per hour by the element at P is NdA and the number passing through the cone is

$$\frac{1}{2} \cdot NdA \left(\frac{R' - x}{R'} \right),$$

where $\frac{R' - x}{R'}$ is the ratio of the solid angle to the upper half of the sphere enclosing the source. Summing over the entire area, assuming R' to be constant,

$$c = \frac{1}{2} \cdot NA \left(\frac{R' - x}{R'} \right). \quad (2)$$

This is linear in x , and becomes zero when $R' = x$. The total number of particles emitted, α , is NA , so that the counting efficiency,

$$\frac{2c}{\alpha} = \left(\frac{R' - x}{R'} \right), \quad (3)$$

and if more than one absorber is present,

$$\frac{2c}{\alpha} = \left(\frac{R' - x_1 - x_2 - \dots - x_n}{R'} \right). \quad (3a)$$

These equations apply to a homogeneous source of alpha-rays*; when a mixture is present emitting alpha-rays of several ranges, it is necessary to apply Equation (3) for each emitter (ranges R'_1, \dots, R'_n), summing and weighting according to their activities, a_1, a_2, \dots, a_n ,

$$\frac{2c}{\alpha} = \frac{\sum \left[a_n \left(\frac{R'_n - x}{R'_n} \right) \right]}{\sum a_n} \quad (3b)$$

Emission from Thin Sources

When the thickness of the radioactive layer reaches measurable dimensions, the absorption of the alpha-rays by the deposit must be taken into account. The simplest case is that of one alpha-emitting substance uniformly distributed in a thin circular layer of base DD' , surface EE' exposed to the counting chamber, and of thickness T_A air-cm., which is less than the effective range for counting, R' (Fig. 1b), and equals h/μ , where h is the actual thickness.

Consider an element P of base area dA and height dy , y air-cm. from the top of the deposit. A cone with vertex at P , base BB' in the exposed surface of the source, and sides of length R' contains all paths of alpha particles which can be counted above the source. Those taking paths outside the cone will be absorbed by the medium. The number of alpha particles emitted per hour by the element at P is Nw or:

$$\mu N \rho dA dy,$$

where N is now the number of alpha particles emitted per gram per hour, ρ the density in grams per cubic centimetre, w the weight in grams, and $dA dy$ the volume of the element. The number passing through the cone and leaving BB' is:

$$\frac{1}{2} \mu N \rho dA dy \left(\frac{R' - y}{R'} \right),$$

where $\frac{R' - y}{R'}$ is the ratio of the solid angle BPB' to the half-sphere which contains all possible paths in the direction of the collecting chamber.

To find the number of alphas, c' , leaving the exposed surface of a column of the source of base dA and height T_A , we integrate between the limits 0 and T_A :

$$c' = \frac{1}{2} \int_0^{T_A} \left[\mu N \rho dA \left(\frac{R' - y}{R'} \right) \right] dy \quad (4)$$

$$c' = \frac{\mu \rho N dA}{2R'} \left(R' T_A - \frac{T_A^2}{2} \right). \quad (4a)$$

* For example, if an extremely thin layer of polonium of range 3.84 air-cm. (and effective range 3.34 air-cm. when the minimum detectable range (discussed later) is 0.5 air-cm.) is deposited on a nickel disc by dipping in a dilute acid solution of a polonium salt, and is placed in a counting chamber covered with an aluminium foil weighing 3.16 mg. per sq. cm., Equation (3) becomes

$$\frac{2c}{\alpha} = \frac{3.34 - 2}{3.34} = 0.4,$$

where thickness,

$$x = \frac{31.6 \times 10^{-4}}{2.7 \times 5.85 \times 10^{-4}} = 2.$$

This is true for any small column, so for the whole surface we may replace dA by A , assuming R' constant over the surface, to obtain the total count, c :

$$c = \frac{\mu \rho N A T_A}{2R'} \left(R' - \frac{T_A}{2} \right). \quad (4b)$$

The total number of rays emitted, α , is given by

$$\alpha = Nw' = \mu N \rho A T_A,$$

so that the counting efficiency is

$$\frac{2c}{\alpha} = \left(1 - \frac{T_A}{2R'} \right), \quad (5)$$

similar to an equation obtained by Finney and Evans in less convenient form (1). It will be noticed that Equation (5) reduces to Equation (3) when $T_A = 0$.

Equation (5) applies in the range $2c/\alpha = 1$ to $\frac{1}{2}$, that is, when T_A is between 0 and R' air-cm.*

Emission When Thickness Exceeds Range of Alpha Particles

When the thickness of the radioactive source is equal to the effective range, $T_A = R'$, the number counted is given by Equation (4b)

$$c = \frac{\mu \rho N A R'}{4}. \quad (6)$$

The count per unit area remains constant as the thickness is increased, since alpha particles emitted below a depth $T_A = R'$ do not reach the surface. However, the measured emission per gram varies inversely with thickness; the fraction of the total emitted rays which are counted becomes smaller according to the relation:

$$c/\alpha = \frac{\rho N A R'}{4 N A T_A \rho} \quad (7)$$

or

$$\frac{2c}{\alpha} = \frac{R'}{2T_A}. \quad (7a)$$

* In counting alpha-rays emitted by thorium (range, 2.60 air-cm.) derived from a uranium-free mineral, Equation (5) becomes

$$\frac{2c}{\alpha} = 1 - \frac{T_A}{4.20},$$

where the effective range is 2.10 air-cm.

The thickness T_A is given by

$$T_A = \frac{1}{\rho \mu} \left(\frac{w'}{A} \right),$$

or more generally, a constant k may be determined experimentally when Equation (5) is expressed in the form

$$\alpha = \frac{2c}{1 - T_A/2R'},$$

so that the activity,

$$a = \frac{\alpha}{w} = \frac{2c/w}{1 - k(w/A)} \text{ alphas/mg./hr.}$$

when w is expressed in milligrams.

At a source thickness equal to the effective range, Equations (5) and (7) reduce to identity:

$$\frac{2c}{\alpha} = \frac{1}{2}.$$

With thick sources, the counting efficiency is proportional to range, while with thin sources it is linear with thickness.

To find the emission per gram, it is not necessary to know the weight when the source thickness exceeds $T_A = R'$ since the measured emission is proportional to area,

$$N = \frac{\alpha}{w'} = \frac{4Kc}{R'A},$$

where K is a constant for the absorbing medium; see Equation (13a).

Minimum Detectable Range and Effective Range

The ranges of alpha-rays are usually measured in air, although the stopping powers of several other substances have been determined with less accuracy. The mean range, R , (the mean of the range of the straggling distribution, Fig. 2) in air at 15° C. and 760 mm. is, therefore, taken as standard (Table II), and the range in other substances, R_0 , is expressed as a function of that quantity:

$$R_0 = \mu R, \quad (8)$$

where μ is the ratio of the range in the medium to the range in air, or the equivalent in the medium of 1 cm. of air, sometimes known as the conversion factor (see Table I).

In practice a certain minimum number of ions must be collected before an alpha-ray pulse is registered by the counting instrument. The minimum quantity of instantaneous ionization which can be detected depends upon the geometry of the source and collecting chamber, the collection potential, and the sensitivity and stability of the amplifier and recording instruments. In the usual type of parallel-plate chambers, about 10,000 ion-pairs represents the observational limit. If an alpha particle travels only the last portion of its range in the chamber air, say, forming 1,000 ion-pairs, it would pass unnoticed. The limiting number of ions required to operate the counter is not a convenient quantity to determine, but because of the similarity in range-ionization curves it may be assumed that this is related to a fixed distance, r , at the end of the path of an alpha-ray. This quantity, r , is termed the *minimum detectable range*.

The effective range of an alpha particle, R' , is therefore $(R - r)$; this is the apparent range for the particular counting instrument.

The relations between mean range in air, R , effective range, R' , minimum detectable ionization, and minimum detectable range, r , are shown diagrammatically in Fig. 2.

The minimum detectable range may be determined experimentally for any counter using Equation (3) or (5) or by interpolation of curves of $2c/\alpha$ versus T_A (or w/A) for several values of r (Figs. 3, 6) where $R = R' + r$, and $N = \alpha/w$ are known. The minimum detectable range usually lies within the range 0.4 to 1.0 air-cm., the actual value depending upon the counting instrument.

TABLE I
ABSORPTION DATA FOR SEVERAL SUBSTANCES

Absorbing medium	Formula used	Density, ρ , gm./cm. ³	Mean square root of atomic weight $\Sigma f\sqrt{W}$	Conversion factor $\mu = \frac{R_0}{R}$	K
Helium				5.88	
Argon				1.02	
Aluminium*				5.85×10^{-4}	
Quartz	SiO ₂	2.65	4.60	5.05×10^{-4}	750
Biotite	HK ₂ Mg ₂ Fe ₂ Al ₂ Si ₂ O ₁₂	3.0	5.37	5.20×10^{-4}	675
Diopside	CaMg(SiO ₃) ₂	3.3	4.86	4.27×10^{-4}	830
Iron pyroxene	MgAlFe ₂ SiO ₆	3.5	5.95	4.92×10^{-4}	700
Hornblende	CaAl ₂ Mg ₂ Fe ₂ Si ₂ O ₁₂	3.3	5.64	4.97×10^{-4}	695
Magnetite	Fe ₃ O ₄	5.17	6.51	3.66×10^{-4}	940
Ilmenite	FeTiO ₃	4.7	6.20	3.83×10^{-4}	900
Albite	NaAlSi ₃ O ₈	2.63	4.61	5.08×10^{-4}	680
Anorthite	CaAl ₂ Si ₂ O ₈	2.75	4.84	5.10×10^{-4}	675
Orthoclase	KAlSi ₃ O ₈	2.57	4.82	5.43×10^{-4}	635
Nepheline	NaAlSi ₃ O ₈	2.60	4.61	5.14×10^{-4}	670
Lepidolite	KLiH ₂ Al ₂ F ₂ Si ₂ O ₁₁	2.85	5.88	6.0×10^{-4}	650
Fluorite	CaF ₂	3.13	5.36	4.97×10^{-4}	675
Cordierite	H ₂ Mg ₂ Fe ₂ Al ₂ Si ₂ O ₁₂	2.62	5.05	5.58×10^{-4}	670
Felsic minerals (F)		2.64	4.68	5.13×10^{-4}	670
Mafic minerals (MF)		3.2	5.45	4.75×10^{-4}	725
Magnetite minerals (M)		4.9	6.4	3.8×10^{-4}	910
Granitic rock (90F + 9MF + 1M)		2.7	4.75	5.1×10^{-4}	675
Basic rock (52F + 45MF + 3M)		3.0	5.1	4.9×10^{-4}	700
Intermediate rock (83F + 15MF + 2M)		2.8	4.8	5.0×10^{-4}	690

* From measurements of pleochroic halos.

Thickness of Deposit

Similarly to the method of expressing range (Equation (8)), the thickness, h , is expressed as the equivalent air thickness, T_A , or as a function of that quantity.

$$h = \mu T_A = \frac{1}{\rho} \left(\frac{w'}{A} \right) \quad (9)$$

or

$$T_A = \frac{1}{\rho\mu} \left(\frac{w'}{A} \right). \quad (10)$$

In the same material ρ and μ are fixed, and if some suitable value of area, A , is selected and can be kept constant, the thickness or T_A term in the preceding equations can be replaced by the weight of the deposit multiplied by a constant (see Equation (13a)). It will be noted that T_A is identical

TABLE II
DATA FOR ALPHA-RAY EMITTERS

Element	Relative activity at equilibrium	Range in air 15° C. 760 mm. Hg.
Uranium I	1	2.65
Uranium II	1	3.21
Ionium	1	3.09
Radium	1	3.26
Radon	1	4.05
Radium A	1	4.66
Radium C	0.0002	4.05
Radium C'	0.9998	6.91
Polonium (RaF)	1	3.84
Actino-uranium	0.0462	3.2
Protoactinium	0.0462	3.63
Radioactinium	0.0462	4.64
Actinium X	0.0462	4.33
Actinon	0.0462	5.63
Actinium A	0.0462	6.46
Actinium C	0.0461	5.36
Actinium C'	0.0001	6.55
Thorium †	1.137	2.10
Radiothorium	1.137	3.95
Thorium X	1.137	4.28
Thoron	1.137	5.00
Thorium A	1.137	5.64
Thorium C	0.398	4.73
Thorium C'	0.739	8.57

† Th/UI assumed to be 3.5.

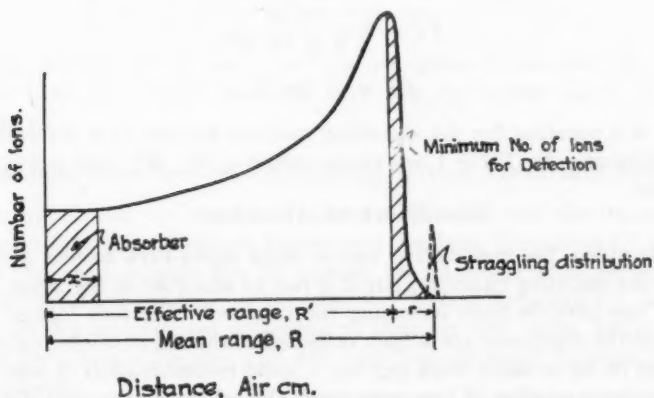


FIG. 2. Range curve for an alpha particle showing the variation in range for one emitter (straggling distribution), the relations between mean range, R , effective range, R' , and minimum detectable range, r .

with the average *stopping power* of the medium. Experiments on the stopping power of various substances have led to the empirical Bragg-Kleeman rule, which fits the data fairly well:

$$\frac{R_1 \rho_1}{R_2 \rho_2} = \frac{\sqrt{W_1}}{\sqrt{W_2}} = \frac{S_2}{S_1}, \quad (11)$$

where R is the range, ρ the density, W the mean atomic weight, S the *mass stopping power* (stopping power divided by density), and the subscripts refer to two different substances. When air at 15°C. and 760 mm. is taken as a standard of reference ($\rho = 1.22 \times 10^{-3}$ and the mean square root of the atomic weights of its elements = 3.76),

$$\mu = \left(\frac{R'_0}{R} \right) \cong \frac{3.25 \times 10^{-4} \sqrt{W}}{\rho}, \quad (12)$$

where $W^{\frac{1}{2}}$ can be obtained from the formula:

$$W^{\frac{1}{2}} = f_1 W_1^{\frac{1}{2}} + f_2 W_2^{\frac{1}{2}} + \dots + f_n W_n^{\frac{1}{2}},$$

where $f_1 \dots \dots \dots f_n$ represents proportion and $W_1 \dots \dots \dots W_n$ atomic weight of the elements, 1, 2, $\dots \dots \dots n$, constituting the molecule.

Accurate measurements of the radii of pleochroic halos have provided a means of obtaining μ for biotite, lepidolite, hornblende, diopside, cordierite, fluorite and some other minerals. These data show that μ calculated by means of Equation (12) is about 10% too high, so that the equation

$$\mu = \frac{2.9 \times 10^{-4} W^{\frac{1}{2}}}{\rho} \quad (12a)$$

is to be preferred (2, 3). For use in the expression for counting efficiency, the following equation is convenient (see Equation (10)):

$$T_A = \frac{w/A}{2.9 \times 10^{-4} W^{\frac{1}{2}}}, \quad (13)$$

$$T_A = K (w/A), \quad (13a)$$

where K is a constant for the absorbing medium and (w/A) is determined by the experiment. In Table I are given values of K , $W^{\frac{1}{2}}$, and μ for several substances.

The Effect of Absorbers

The air above the radioactive source stops alpha-rays having a residual range in the counting chamber, but it is not an absorber in the sense that it prevents the particle from operating the counter. The ions formed in the air-path of the alpha-ray are largely collected at the negative electrode under a gradient of 45 or more volts per cm. Some recombination of ions occurs and a minimum number of ions must reach the collector to cause a detectable current or to change appreciably the capacity of the system by momentarily changing the dielectric constant of the medium. The minimum detectable

range, r , is not comparable to an absorber thickness, in that the ray does not have to pass through a layer of thickness r air-cm. but only to travel a distance r in the chamber nearly independent of direction.

The effect of an absorber of thickness x in reducing the alpha-ray emission into the chamber is greater than that of an equivalent air thickness of deposit, since the latter is a source of alpha-rays while the absorber is not. Actually, integration of Equation (4) between the same limits as before when y is replaced by $(y + x)$ shows absorbers to have twice the effective stopping power of an equivalent thickness of deposit.

In the case of a deposit covered by an absorber, then, T_A in the previous equations must be replaced by $T_A + 2x$. In the general case of m absorbers of the thicknesses x_1, x_2, \dots, x_m , the equation for thin sources is,

$$\frac{2c}{\alpha} = 1 - \frac{T_A + 2x_1 + 2x_2 + \dots + 2x_m}{2R'}, \quad (14)$$

which applies only when $T_A + \Sigma x_m$ is less than R' .

In thick sources, the emission per unit area of surface is constant, the rate being given by the equation for thin sources (Equation (4b)) in the limiting case, that is, when the effective range $R' = T_A + x$. Substituting $T_A = R' - x$ for the source thickness in Equation (4b), the number of countable rays from sources where the source thickness plus absorber thickness exceeds R' is given by

$$c = \mu \rho \frac{NA}{4R'} (R'^2 - x^2), \quad (15)$$

and since $\alpha = \mu \rho NA T_A$, the counting efficiency is given by

$$\frac{2c}{\alpha} = \frac{1}{2T_A} \left(\frac{R'^2 - x^2}{R'} \right), \quad (16)$$

or in the general case of m absorbers (Equation (3a))

$$\frac{2c}{\alpha} = \frac{1}{2T_A} \left[\frac{R'^2 - (x_1 + x_2 + \dots + x_m)^2}{R'} \right], \quad (16a)$$

where the thicknesses of the absorbers are given in air-cm.; x_m may be obtained from the actual thickness x_m if the conversion factor is known, $x'_m = \mu_m x_m$.

Emission from Sources Containing Several Alpha-Ray Emitters

When more than one alpha-ray emitter is present, and the relative rates of emission (activity ratios) are known and constant, Equations (5) and (7a) for thin and thick sources can be applied, the choice of equation depending upon whether T_A is less than, or exceeds, R' . $2c/\alpha$ is computed for each emitter, the results are weighted according to their activity ratios, and averaged. Both of the above equations give the counting efficiency in terms of range and thickness:

$$\frac{2c}{\alpha} = f(R', T_A).$$

If R'_1, R'_2, \dots, R'_n are the ranges of the emitters of activities, N_i ,

N_2, \dots, N_n , c is the observed count, and α is the total emission, the over-all counting efficiency is obtained as follows:

$$\frac{2c}{\alpha} = \frac{\sum N_i f(R'_i, T_A)}{\sum N_i} \quad (17)$$

where $f(R', T_A) = 1 - \frac{T_A}{2R'}$, when $T_A < R'$,

and $f(R', T_A) = R/2T_A$, when $T_A > R'$.

When the activity ratios are not known, or the relative rates of emission are changing with time, the method summarized by Equation (17) cannot be used. In the simplest case, where the emission rates of two emitters are constant, the relative activities may be determined by means of counting experiments with absorbers. When the rates are changing it is necessary to determine the change of count with time, t , making use of the fundamental equation for radioactive disintegration.

$$\frac{dc}{dt} = e^{-\lambda t}$$

Alpha-Ray Emission from Rocks

The determination of the alpha-ray activity of rocks and minerals is important in geothermal problems and in attempts to determine geological age. The alpha-ray activity provides a direct measure of the present rate of generation of helium,

$$a = 0.104 \text{ Ra} + 0.0886 \text{ Th alphas/mg./hr.}$$

and of the heat produced in typical rocks ($\text{Th/UI} = 3.5$, $K/a = 2.06$)

$$H = 2.25a \text{ cal./gm./million years.}^*$$

Of the 25 alpha-ray emitters in terrestrial materials, samarium, actinium C', and radium C produce a small enough proportion of the alpha-rays to be neglected.

The remaining 22 contribute to the emission to an extent determined by their rates of decay, relative concentration, the source thickness, and range. Usually the thorium and uranium series each account for a little less than half of the activity, while the actino-uranium series is responsible for a few per cent of the total activity.

As most rocks are older than one million years, the radioactive series are in equilibrium and the rate of alpha-ray production is the same for each alpha-ray emitter in a series (or group of emitters in the case of branching). The uranium and actino-uranium series are also related, since their decay constants are known and their isotopic abundances have been determined ($\text{UI} = 139 \text{ AcU}$) (5).

* Where Ra is expressed in 10^{-12} gm./gm., Th in 10^{-8} gm./gm., and the ratios of concentrations of thorium, Th, uranium, UI, polonium, K, in gm./gm., and activity, a, in alphas per mg. per hr. are assumed to be constant for purposes of calculation.

If the activities of the members of the uranium series are taken as unity, the relative activities of the actino-uranium series are given by the activity ratio

$$\frac{N_{AcU} \lambda_{AcU}}{N_{UI} \lambda_{UI}} = 0.046 \pm 0.002,$$

and if Th/UI is assumed to be 3.5, the relative activities of the thorium series are given by $3.5 \frac{\lambda_{Th}}{\lambda_{UI}} = 1.138^*$. Values of the activities relative to that of uranium as unity and using Th/UI = 3.5 are given in Table II, Column 2.

Errors due to variations in the true thorium-uranium ratio from 3.5 are small enough to be neglected in absorption theory, in the rate of helium production, and in the rate of heat production. In Fig. 3 the change of $2c/\alpha$ with T_A for samples containing all thorium or all uranium are compared with one for which Th/UI = 3.5. It is clear (4) that normal variations in the Th/UI ratios of rocks introduce negligible error if this ratio is assumed to be 3.5.

To calculate the true emission from observed alpha-rays emitted from rock films it is necessary to apply Equations (5) and (7a), following the method summarized by Equation (16). This procedure may be simplified by using a graphical method of calculation. Resultant values of $2c/\alpha$ obtained in this way are shown as a function of T_A in Fig. 4 for several values of minimum detectable range. In shape, these curves are similar to, but not identical with, those for pure alpha-rays. The portion of the curves in the range of $2c/\alpha$ between 1.0 and 0.5 are nearly linear, closely approximating the curves for a range of 3.8 air-cm.

The curves for thicker deposits approximate curves for a range of 4.3 air-cm., which is equal to the average weighted range (sum of Column 3 divided by the sum of Column 2, Table II); this is to be expected for thick deposits since average emission is constant and solely dependent upon range. Actually the relation does not become exact until the thickness exceeds the effective range for counting alpha-rays from ThC', those with greatest energy. With thinner layers, $2c/\alpha$ is less than that computed. This can be shown simply when there are two ranges $R_A + dR$ and $R_A - dR$. The "apparent range" is less than the average range, R_A , by a factor $\frac{R_A^2 - dR^2}{R_A^2}$ and the counting efficiency,

$$\frac{2c}{\alpha} = 1 - \frac{T_A}{2R_A} \frac{R_A^2}{R_A^2 - dR^2}. \quad (18)$$

When T_A is less than $R_A - dR$, $2c/\alpha$ is a linear function of T_A with an apparent range of $\frac{R_A^2 - dR^2}{R_A}$; when T_A exceeds $R_A - dR$ the emission is constant, and the change of $2c/\alpha$ with T_A given by Equation (7):

$$\frac{2c}{\alpha} = \frac{R_A}{2T_A}.$$

* In the case of ThC, 35% produces ThC', with the emission of an alpha-ray of range 4.73 air-cm., and 65% disintegrates into ThC', which in turn emits an alpha-ray of range 8.57 cm.

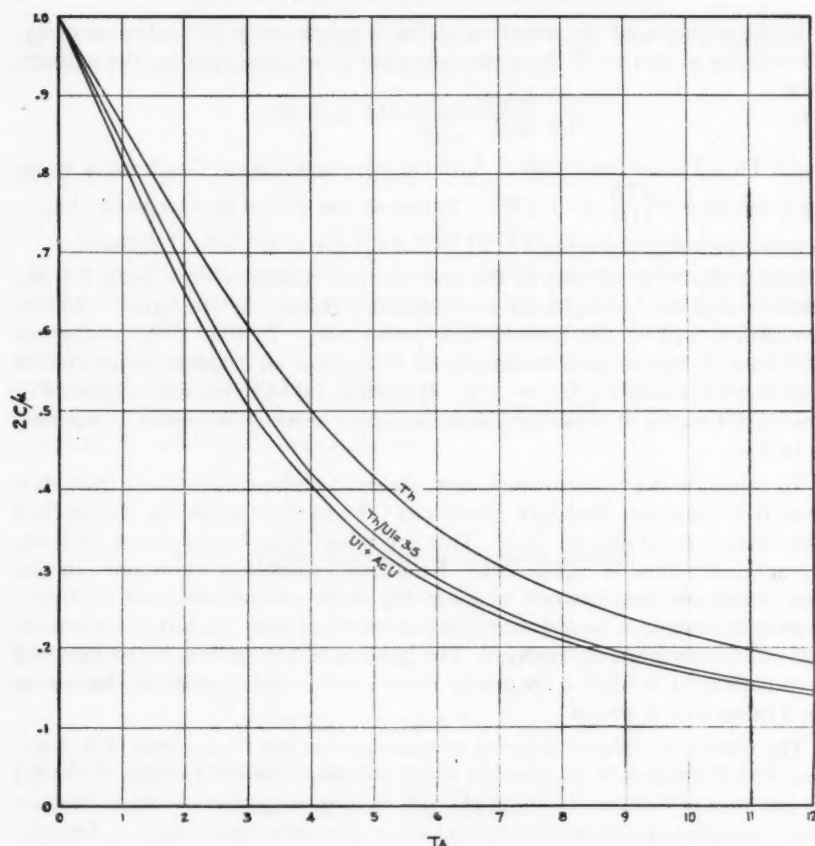


FIG. 3. Change in $2c/\alpha$ with T_A for the thorium and uranium series and for a mixture in which $Th/UI = 3.5$.

In the range between $R_A + dR$ and $R_A - dR$, the apparent range changes with T_A so that no single equation can be applied. However, for rocks, two equations can be employed using $R = 3.83$ for $T_A = 0$ to 4 (Equation (19a)) and $R = 4.30$ when T_A exceeds 4 or w/A exceeds 6 (Equation (19b)), without introducing errors any greater than present experimental errors (Fig. 5).

Using $K = 690$ (Equation (13a), Table I) and $r = 0.5$ air-cm., and expressing the weight in milligrams, these equations are, for $w/A < 6$:

$$\frac{2c}{\alpha} = 1 - \frac{0.690 (w/A)}{2(3.83 - 0.5)}$$

$$a = \frac{\alpha}{w} = \frac{2c/w}{1 - 0.1 (w/A)} \text{ alphas/mg./hr.} \quad (19a)$$

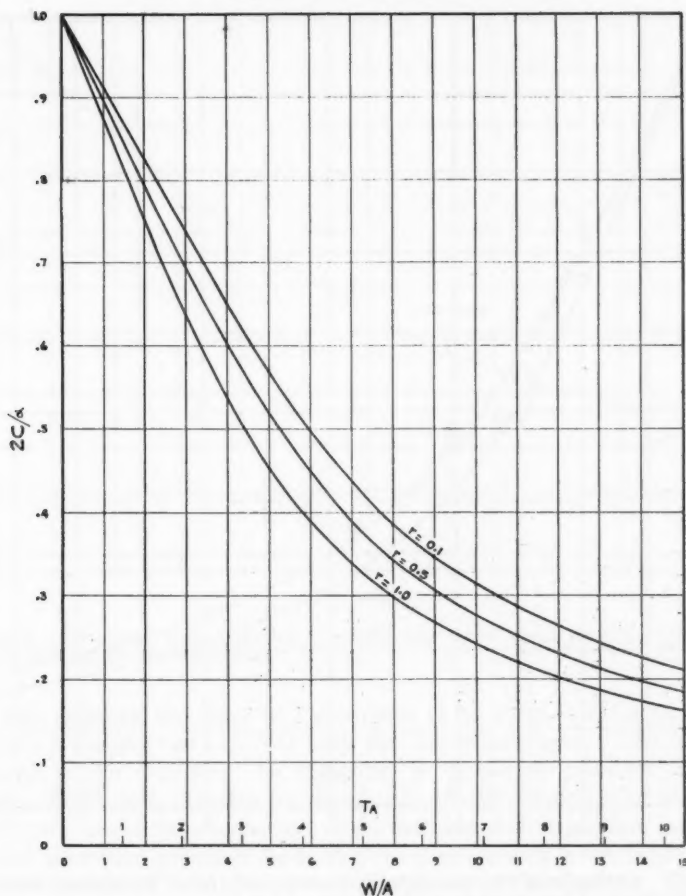


FIG. 4. Effect of thickness (T_A , w/A) on counting efficiency ($2c/\alpha$) at three values of minimum detectable range.

and for $w/A > 6$:

$$\frac{2c}{\alpha} = \frac{3.80}{2 \times 0.690(w/A)}$$

$$a = \frac{\alpha}{w} = 0.72 \text{ } c/A \text{ alphas/mg./hr.} \quad (19b)$$

and if the area is constant, say 72 sq. cm., the alpha-emission per gram per hour is merely 10 times the observed count.

In more general form, Equations (19a) and (19b) may be written:

$$a = \frac{2c/w}{1 - k_1(w/A)} \quad (19c)$$

$$a = k_2 c/A. \quad (19d)$$

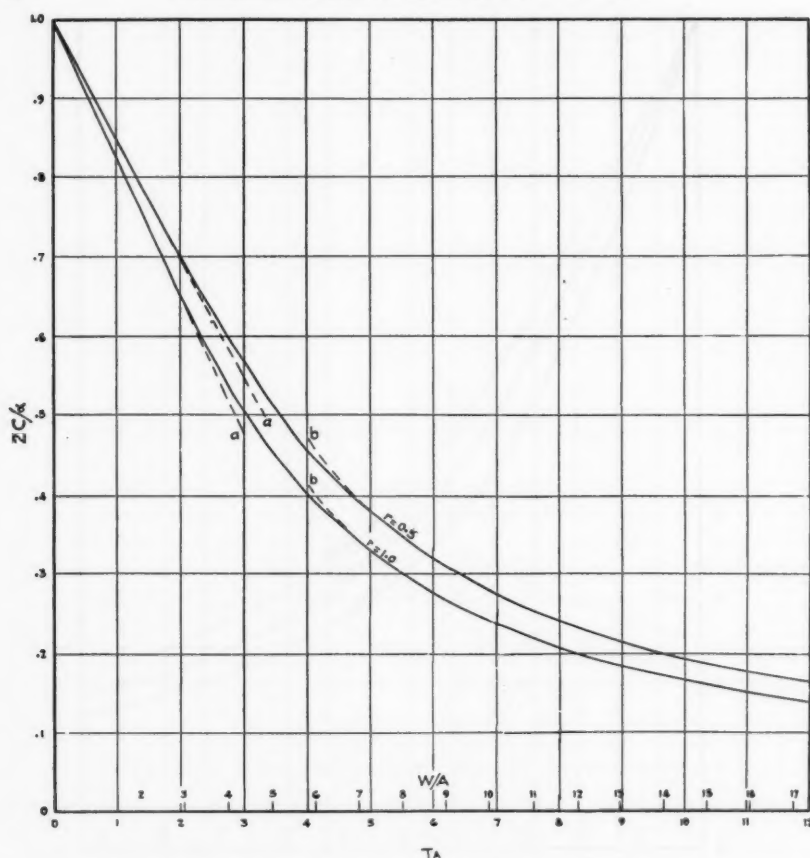


FIG. 5. Application of Equations (19a) ("a" curves) and (19b) ("b" curves) at two values of r , and deviations from actual curves (solid) near $w/A = 5$.

From the discussion of minimum detectable range it is clear that k_1 and k_2 depend upon the type of collecting instrument and must be determined experimentally. This can be accomplished either by using absorbers and a uniform source of alpha-rays to obtain minimum detectable range, or by determining c at several values of (w/A) and obtaining α by extrapolation, or preferably by using a sample for which the radium and thorium contents are known either from analysis or synthesis. The minimum detectable range in parallel-plate chambers is usually close to 0.5 air-cm. and can be determined by absorption experiments from a pure alpha-ray emitter such as polonium.

Experimental tests of the above equations have been made using a sample of Quincy granite which had been studied previously by radon, thoron, and alpha-counting techniques. The results are summarized in Fig. 6.

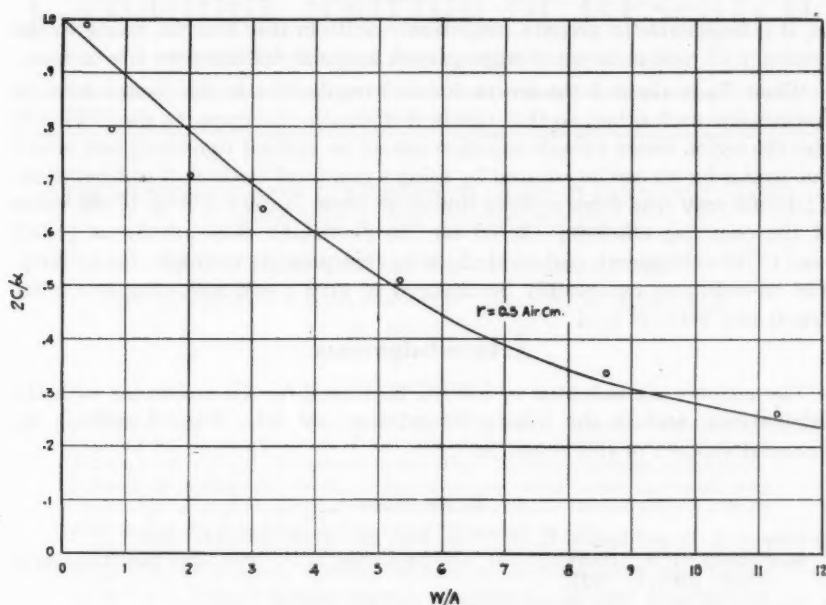


FIG. 6. Comparison of the theoretical curve with experimental results for a granite; circles show experimentally determined values.

With thin deposits, the value of $2c/\alpha$ tends to be lower, while with thicker sources it is higher than expected from the theoretical curve. This is easily explained if one considers the difficulty in preparing perfectly uniform sources. With thick deposits the emission is purely a function of area, and examination, under the microscope, of the surfaces of rock powders deposited on metal discs from solutions shows that the effective area is somewhat higher than that calculated from the over-all dimensions of the deposit. Thus too low a value of A is used, which tends to yield too high a value of $2c/\alpha$. Equation (19b) is independent of the density of the source, so that the difficulties discussed by Finney and Evans (1) do not enter.

With thin deposits, on the other hand, it is not the surface area of the source but the source thickness which is the determining factor. It is extremely difficult to prepare perfectly uniform thin layers of rock samples, so that irregularities in thickness are the rule rather than the exception. Microscopic studies of thin deposited layers of rock have shown that ordinary grinding may leave grains which are thicker than the average source thickness as given by $w/\rho A$. Thus there is greater absorption of alpha-rays than indicated by Equation (5) and too low a value of $2c/\alpha$ results. Obviously finer grinding in agate mortars circumvents this difficulty to some extent, and the writers have had best success with final grinding using a lubricant such as alcohol preparatory to dispersion in the fluid and deposition on the metal disc. Even

so, it is impossible to prepare consistently uniform thin sources, owing to the tendency of rock minerals to aggregate in irregular fashion over the surface.

When T_A is about 4 the errors due to irregularities in the source tend to compensate each other, so that this is a desirable thickness to use. This is also the region where a single equation cannot be applied rigorously but errors due to this factor can be reduced by using a graphical method of computation. Thus one may read from a curve similar to those in Figs. 3, 4 or 6, the value of the counting efficiency ($2c/\alpha$) for the particular value of T_A or (w/A) used in the experiment, and divide $2c/w$ by this quantity to obtain the activity. The co-ordinates can readily be changed to give a multiplicative factor for c/w at any value of w/A .

Acknowledgments

The authors are indebted to Mr. A. R. Keevil for his assistance with the calculations, and to the Viking Foundation and Mr. Hans Lundberg for financial support of this research.

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THE SYNTHESIS OF 2-KETOCYCLOHEXYLSUCCINIC ACID AND RELATED SUBSTANCES

II. SYNTHESSES INVOLVING CYCLOHEXANONE¹

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H. M. MACFARLANE⁴

Abstract

2-Ketocyclohexylacetic acid and 2-ketocyclohexyl- α -propionic acid were prepared by the condensation of the sodio-derivative of ethyl cyclohexanone-2-carboxylate with ethyl bromoacetate and ethyl α -bromopropionate, respectively, followed by hydrolysis. This method of condensation is not successful with ethyl α -bromo- β -phenylpropionate. It also fails with α -bromo-esters of dibasic acids such as ethyl bromomalonate and ethyl bromosuccinate.

The γ -lactones of cyclohexanolacetic acid and cyclohexanol- α -propionic acid result from Reformatsky reactions between cyclohexanone and ethyl bromoacetate and ethyl α -bromopropionate, respectively, followed by treatment with mineral acid. Ethyl bromomalonate and ethyl bromosuccinate fail to react with cyclohexanone in either Reformatsky or Grignard reactions.

Introduction

The synthesis of 2-ketocyclohexylsuccinic acid and related substances from cyclohexene oxide by McRae, Charlesworth, and Alexander (23) is somewhat involved, and in the case of 2-ketocyclohexylbenzylacetic acid requires a long period of refluxing for the reaction to occur. In a search for simpler methods and also to confirm the structures assigned, synthetical work starting with cyclohexanone was begun.

Four methods seemed to suggest themselves:

1. The elimination of sodium bromide between the sodio-derivative of ethyl cyclohexanone-2-carboxylate and brominated esters, followed by hydrolysis.
2. The oxidation of the γ -lactones of cyclohexanol carboxylic acids which are prepared by Reformatsky reactions between cyclohexanone and α -brominated esters, followed by treatment with mineral acid.
3. As 2, except that the γ -lactones are produced by the action of Grignard reagents on cyclohexanone.

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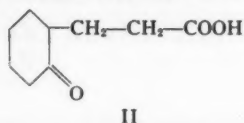
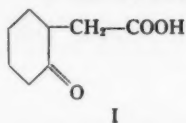
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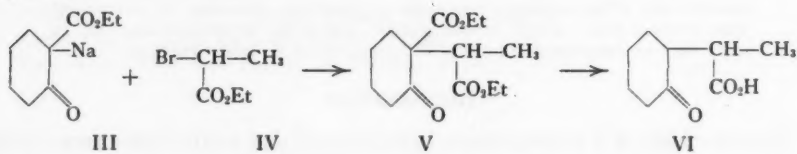
4. The condensation of 2-bromocyclohexanone with the sodio-derivative of the proper substituted malonic ester.

Method 1

Chuang and Ma (4), Chatterjee (3), and Ghosh (14) have synthesized 2-ketocyclohexylacetic acid (I) from ethyl cyclohexanone-2-carboxylate and ethyl chloroacetate. We have repeated this preparation, employing ethyl bromoacetate, and have obtained a purer product than that prepared by the other authors and by ourselves (23). This method has been employed in



the synthesis of 2-ketocyclohexyl- β -propionic acid (II) by Openshaw and Robinson (25), F. Lions (21), and Haworth and Mavin (15). A synthesis of the corresponding 2-ketocyclohexyl- α -propionic acid (VI) resulted when the sodio-derivative of ethyl cyclohexanone-2-carboxylate (III) was condensed with ethyl α -bromopropionate (IV) and the resulting ester (V) subjected to hydrolysis.



In a previous communication (23), we described the preparation of the lactone of cyclohexanolbenzylacetic acid and 2-ketocyclohexylbenzylacetic acid in the form of its lactone. In an attempt to produce these substances by Method 1 the writers condensed the sodio-derivative (III) with ethyl α -bromo- β -phenylpropionate, expecting the ester (VII), and on hydrolysis 2-ketocyclohexyl- β -phenylpropionic acid (VIII).



The oil resulting from the condensation had a composition in fair agreement with that of the ester (VII), but molecular weight determination and the production of cinnamic acid from it by the action of mineral acid proved it to be ethyl α -hydroxy- β -phenylpropionate. It would appear that the ester (VII) has not been formed and that the α -hydroxy- β -phenylpropionic ester resulted from the action of the alkaline condensing medium on the bromo-ester. This is in agreement with the work of E. Fischer and Zemlén (13)

who prepared inactive α -hydroxy- β -phenylpropionic acid from the corresponding bromo-acid by heating with water and calcium carbonate, and of McKenzie and Wren (22) who report the preparation of the active acids from the active bromo-acids by the action of alkali and by water alone.

The main interest has centred in the application of this method to the attempted preparation of 2-ketocyclohexylmalonic acid and 2-ketocyclohexylsuccinic acid. When ethyl cyclohexanone-2-carboxylate was condensed with ethyl bromomalonate it was expected that the ester (IX) would result, and, on hydrolysis, 2-ketocyclohexylmalonic acid (X).



Again it would appear that the reaction did not occur when metallic sodium in benzene was used as the condensing agent, as the original reactants were recovered unchanged, along with an oil, probably ethanetetra-carboxylic ester, as on hydrolysis it produces succinic acid. The ethanetetra-carboxylic ester results from the action of two atoms of sodium on two moles of the bromomalonate ester. Ethanetetra-carboxylic ester was made in a somewhat similar manner from sodiomalonate ester and bromine by Kötze and Stalman (20), from chloromalonate ester and sodiomalonate ester by Conrad and Bischoff (6), from 1 : 2-dibromocyclohexane and ethyl sodiomalonate by Coffey (5), and from bromomalonate ester with sodium iodide in acetone by Finkelstein (12).

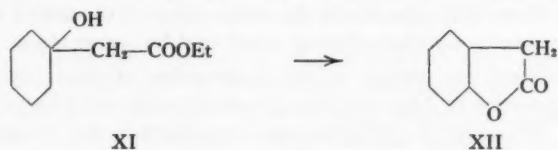
When sodium ethylate was used as the condensing agent in place of metallic sodium, monobromoethanetetra-carboxylic ester and ethylenetetra-carboxylic ester were isolated. Conrad and Brückner (7) reported the preparation of ethylenetetra-carboxylic ester by the action of sodium on dibromomalonate ester in benzene, and Curtiss (10), used the action of sodium ethylate on dibromomalonate ester. Conrad and Guthzeit (8, 9) reported its formation by the action of either sodium or sodium ethylate on chloromalonate ester. The monobromoethanetetra-carboxylic ester formed was apparently an intermediate in the formation of the ethylenetetra-carboxylic ester.

This reaction failed also with ethyl cyclohexanone-2-carboxylate and monobromosuccinic ester. The products resulting have not been identified, but no 2-ketocyclohexylsuccinic acid has been obtained.

Method 2

Reformatsky reactions have been utilized in the preparation of α -(1-cyclohexanol) fatty acid esters by Wallach and his associates (28, 29, 30) and by Auwers and Ellinger (1). C. H. Boehringer Sohn A.-G. (2) have prepared the γ -lactones of cyclohexanol fatty acids by boiling these esters with mineral acids. From cyclohexanone, ethyl bromoacetate, and zinc we have obtained the hydroxy ester (XI) and on treatment with mineral acid the γ -lactone of

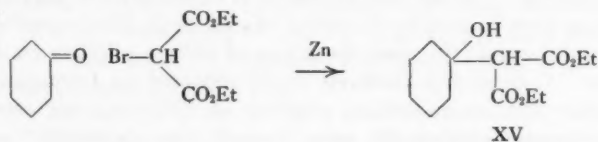
cyclohexanolacetic acid (XII) identical in properties with that prepared by Coffey (5) and with that reported in our previous communication (23).



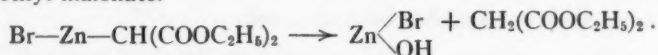
Similarly from cyclohexanone and ethyl α -bromopropionate there was produced the hydroxy ester (XIII), which, with mineral acid, gave the γ -lactone of cyclohexanol- α -propionic acid (XIV).



Although Reformatsky reactions with α -halogenated esters of monocarboxylic acids are fairly common, there appear to be only two recorded cases of the use of α -halogenated esters of dibasic acids in this reaction. In both cases esters of bromomalonic acid were employed. Kohler, Heritage, and Macleod (17) report that, using unsaturated ketones and methyl bromomalonate, 1 : 4-addition occurs. Iyer (16) attempted Reformatsky reactions using acetone and ethyl bromomalonate, and found that water was eliminated between two molecules of acetone, yielding mesityl oxide, and this was followed by 1 : 4-addition. In the hope of preparing the hydroxy ester (XV) we have applied the Reformatsky reaction to cyclohexanone and bromomalonic ester under a variety of conditions. In no case did the reaction proceed.



It would appear that there was formed, between the zinc and the bromomalonic ester, a complex similar to a Grignard reagent, which on acidification gave ethyl malonate.



This complex apparently did not react with the cyclohexanone, or only very slightly, as the latter was recovered. In one case, when a large excess of zinc was employed, ethanetetra-carboxylic ethyl ester was obtained, apparently by removal of bromine between two molecules of bromomalonic ester.

In similar reactions between ethyl monobromosuccinate and cyclohexanone nothing but ethyl succinate could be isolated.

Method 3

Following failure of the ethyl bromomalonate to react with cyclohexanone in the Reformatsky reaction an attempt was carried out with the Grignard reaction. The cyclohexanone failed to react and was recovered along with ethanetetra-carboxylic ester.

It would appear that the α -brominated dicarboxylic esters are not nearly so reactive in Reformatsky and Grignard reactions as the corresponding esters of the α -bromo-monocarboxylic acids. Further experiments with esters of α -bromo-dicarboxylic acids and other ketones and aldehydes in place of cyclohexanone are in progress.

Method 4

One attempt only has been made by this method. 2-Bromocyclohexanone was condensed with the sodio-derivative of the triethyl ester of propane- α,α,γ -tricarboxylic acid. Hydrolysis and heating to decarboxylate failed to yield α -(2-ketocyclohexyl) glutaric acid or any other pure material.

Experimental

Ethyl bromomalonate, b.p. 121 to 125° C. (16 mm.)*, was prepared by the method of Palmer and McWherter (26) from diethyl malonate. Yields up to 75% of the theoretical were obtained.

Ethyl bromosuccinate. Attempts to brominate ethyl succinate by the previous method gave such low yields that the following modification of the method of Volhard (27) was employed. Succinic acid (118 gm.) was mixed with red phosphorus (20 gm.) in a 1-litre, three-necked flask fitted with a reflux condenser, stirrer, and two dropping funnels. Bromine (240 gm.) was slowly run in, the original reaction being moderated by the simultaneous addition of carbon tetrachloride (75 to 100 cc.). After the addition of the bromine, the mixture was heated on the water-bath until the colour of the bromine had disappeared. Twice the calculated quantity of absolute alcohol was slowly dropped in and the heating continued for half an hour. After removal of the carbon tetrachloride and excess alcohol the ethyl bromosuccinate (88 gm.) was distilled at 125 to 128° C. (24 mm.).

2-Ketocyclohexylacetic Acid (I)

Ethyl cyclohexanone-2-carboxylate (40 gm.), b.p. 130 to 140° C. (19 mm.), prepared by the method of Kötze, Michels, and Götz (18, 19), and finely divided sodium (5.3 gm.) were refluxed with dry benzene (150 cc.) until the evolution of hydrogen had ceased (about four hours). Ethyl bromoacetate (38 gm.) was then slowly added and the mixture refluxed five hours on the water-bath. The mixture was cooled, acidified with dilute sulphuric acid, and the benzene layer washed with water and dilute sodium bicarbonate solution and dried over calcium chloride. The benzene was removed and the ethyl cyclohexanone-2-carboxy-2-acetate (19 gm.) distilled under reduced pressure; b.p., 195 to 210° (45 mm.).

*Boiling points and melting points are uncorrected.

Ethyl cyclohexanone-2-carbethoxy-2-acetate (19 gm.) was refluxed eight hours with twice its volume of concentrated hydrochloric acid. The mineral acid was distilled under reduced pressure and the 2-ketocyclohexylacetic acid was purified by distillation; b.p. 190 to 195° C. (30 mm.). On prolonged cooling, the oil (8 gm.) partially solidified. The solid was separated from the oil and crystallized from hexane. The 2-ketocyclohexylacetic acid thus obtained melted at 75 to 78° and was identical with that previously reported by the writers (23). Found: C, 60.3; H, 8.08%; equivalent weight, 153.5. Calc. for $C_8H_{12}O_3$: C, 61.5; H, 7.69%; equivalent weight, 156.

The phenylhydrazone of this keto acid prepared in the usual way melts at 162 to 163°.

2-Ketocyclohexyl- α -propionic acid (VI)

Sodium (3.3 gm.) was dissolved in absolute alcohol (83 cc.) and to the solution a mixture of ethyl cyclohexanone-2-carboxylate (25 gm.) and ethyl α -bromopropionate (26.7 gm.) was gradually added. The mixture was heated for four hours on the water-bath and then poured into cold water (400 cc.). A brown oil separated; it was taken up in ether and dried over sodium sulphate. After removal of the ether, the residue was distilled, the ethyl cyclohexanone-2-carbethoxy-2- α -propionate (17 gm.) boiling at 180 to 190° C. (17 mm.). Found: C, 61.4; H, 7.94%. Calc. for $C_{14}H_{22}O_6$: C, 62.2; H, 8.15%.

To ethyl cyclohexanone-2-carbethoxy-2- α -propionate (15 gm.) was added concentrated hydrochloric acid (60 cc.), and the mixture was allowed to stand overnight, and then refluxed for one hour. The greater part of the mineral acid was distilled under reduced pressure and a saturated solution of ammonium sulphate was added. The oil separating was taken up in ether and the acid fraction removed by washing with dilute sodium hydroxide. On acidification and extraction, a brown oil was obtained, which partially solidified on prolonged cooling. The solid was separated from the oil and boiled with petroleum ether. On cooling, a pale yellow solid (0.5 gm.), m.p. 103 to 105° C., was obtained. Found: C, 62.7; H, 8.3%; equivalent weight, 177. Calc. for 2-ketocyclohexyl- α -propionic acid, $C_9H_{14}O_3$: C, 63.5; H, 8.23%; equivalent weight, 170. Despite the lower melting point, this is undoubtedly an impure sample of the same acid (m.p., 134 to 135°) previously reported by the writers (23).

Attempted Preparation of 2-Ketocyclohexyl- β -phenylpropionic Acid (VIII)

Ethyl α -bromo- β -phenylpropionate, prepared by the method of Marvel (24), was condensed with ethyl cyclohexanone-2-carboxylate in the manner just described for ethyl cyclohexanone-2-carbethoxy-2- α -propionate. Other than some recovered starting materials, the only product isolated was a pale yellow oil boiling at 148 to 150° C. (15 mm.). This was not the expected ester (VII), but proved to be ethyl α -hydroxy- β -phenylpropionate, whose boiling point is reported by Findlay and Hickmans (11) as 156° (20 mm.). Found: C, 68.5; H, 8.1%. Calc. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.22%. Calc. for ester (VII), $C_{20}H_{26}O_4$: C, 69.4; H, 7.51%.

When this oil was treated in the usual manner with concentrated hydrochloric acid, a solid was obtained, which, on crystallization from water, melted at 132 to 133° C. and proved to be cinnamic acid (mixed melting point showed no depression). Found: C, 73.1; H, 5.84%; equivalent weight, 146.9. Calc. for $C_9H_{10}O_2$: C, 72.9; H, 5.4%; equivalent weight, 148.

Attempted Preparation of 2-Ketocyclohexylmalonic Acid (X)

When ethyl cyclohexanone-2-carboxylate (40 gm.) and ethyl bromomalonate (57 gm.) were condensed with sodium (5.3 gm.) in dry benzene (200 cc.) by the method described above for ethyl cyclohexanone-2-carbethoxy-2-acetate, besides unchanged starting materials, there was obtained a yellow oil (15 gm.) boiling at 200 to 210° C. (21 mm.), which was probably ethyl ethane-tetracarboxylate whose boiling point is recorded as 200 to 210° (8 mm.). Confirmation of this view was afforded when the oil was treated with concentrated hydrochloric acid in the usual manner. The residue on crystallization from acetic acid proved to be succinic acid, m.p. 187 to 188°.

When the condensation was carried out in alcohol with sodium ethylate as the condensing agent a reddish oil boiling at 190 to 220° C. (16 mm.) was obtained. Crystals separated on standing and cooling and were filtered from the remaining oil. On repeated crystallization from ligroin, white prisms, m.p. 54 to 55° were obtained. These are probably ethylenetetracarboxylic ethyl ester whose m.p. is given as 58° by Conrad and Guthzeit (8, 9). Found: C, 53.0; H, 7.04%. Calc. for $C_{14}H_{22}O_8$: C, 52.8; H, 6.92%. The oil from which the crystals separated was redistilled (b.p. 210° (14 mm.)); it contained bromine and is probably monobromoethanetetracarboxylic ethyl ester. Found: Br, 20.4%; mol. wt. (ebullioscopic in benzene), 309. Calc. for $C_{14}H_{23}O_8Br$: Br, 20.2%; mol. wt., 399.

When ethyl cyclohexanone-2-carboxylate and ethyl bromosuccinate were condensed in alcohol in the presence of sodium ethylate, a colourless oil boiling at 237° C. (10 mm.) was obtained which has not been identified. Found: C, 58.3; H, 8.47%. On treatment of this oil with concentrated hydrochloric acid and crystallization from acetic acid, a small amount of an acid, m.p. 102 to 103°, and of equivalent weight 63.3 was obtained. This acid has not been identified but was definitely not 2-ketocyclohexylsuccinic acid.

Reformatsky Reactions

(a) γ -Lactone of Cyclohexanolacetic Acid (XII)

Cyclohexanone (25 gm.), ethyl bromoacetate (42 gm.), and zinc (16 gm.) were refluxed in dry benzene (125 cc.) on the water-bath, until virtually all the zinc had dissolved (two hours). After cooling, the mixture was acidified with dilute sulphuric acid and the benzene solution washed with water and dilute sodium bicarbonate solution and dried over sodium sulphate. The benzene was distilled off and the ethyl 1-cyclohexanolacetate (20 gm.) distilled *in vacuo*; b.p. 143 to 146° C. (37 mm.), in agreement with the figure 141° C. (33 mm.) recorded by Auwers and Ellinger (1).

Ethyl 1-cyclohexanolacetate (20 gm.) was heated for nine hours with twice its volume of concentrated hydrochloric acid. The solution was extracted with ether, the extract washed with dilute sodium carbonate solution, then with water, and dried over sodium sulphate. After removal of the ether the γ -lactone of the cyclohexanolacetic acid (5 gm.) distilled at 152 to 156° C. (28 mm.) Found: C, 67.9; H, 8.96%. Calc. for $C_8H_{12}O_2$: C, 68.57; H, 8.57%.

(b) *γ -Lactone of Cyclohexanol- α -propionic Acid (XIV)*

Cyclohexanone (25 gm.), ethyl α -bromopropionate (46 gm.), and zinc (16 gm.) in benzene (125 cc.) were treated in a Reformatsky reaction as above. Ethyl α -(1-cyclohexanol) propionate (28 gm.) was obtained as a colourless oil boiling at 140 to 143° C. (23 mm.). Auwers and Ellinger (1) record 127° (16 mm.) and Wallach and Evans (28) 135 to 136° (20 mm.). When this ester (20 gm.) was refluxed for nine hours with twice its volume of concentrated hydrochloric acid, extracted with ether, and washed with sodium carbonate solution as above, the γ -lactone of cyclohexanol- α -propionic acid was obtained as a colourless sweet smelling oil (5.5 gm.) boiling at 150° (21 mm.). This boiling point is in agreement with that recorded by the writers (23) when the product is prepared from cyclohexene oxide. Found: C, 69.8; H, 9.54%. Calc. for $C_9H_{14}O_2$: C, 70.1; H, 9.09%.

(c) *Attempted Reformatsky Reactions with Cyclohexanone and Ethyl Bromomalonate or Ethyl Bromosuccinate*

Cyclohexanone (41 gm.), ethyl bromomalonate (100 gm.), and zinc* (42 gm.) were refluxed in dry benzene (200 cc.). After half an hour a vigorous reaction set in. When this had moderated, refluxing was continued for one hour. The mixture was acidified with dilute sulphuric acid and the benzene layer washed with dilute sodium bicarbonate solution, then water, and dried over sodium sulphate. After removal of the benzene the remaining oil was distilled *in vacuo* and, besides some unchanged cyclohexanone and ethyl bromomalonate two fractions were obtained: I. Colourless oil (40 gm.), b.p. 106 to 108° C. (35 mm.). II. Reddish oil (4 gm.), b.p. 150 to 165° (25 mm.). Fraction I has been identified as ethyl malonate. Found: C, 53.7; H, 7.57%. Calc. for $C_7H_{12}O_4$: C, 52.5; H, 7.5%. With strong ammonia it gave a white solid, m.p. 170°, with no depression of melting point when mixed with an authentic sample of malonamide.

Fraction II has not been identified and while the colour and boiling range indicated that it could not be quite pure the high carbon content showed that it was not the desired ethyl 1-cyclohexanolmalonate (XV), $C_{13}H_{22}O_5$, which requires C, 60.5; H, 8.56%. Found: C, 70.28; H, 8.58%.

This reaction has been carried out several times employing various conditions and proportions of reactants but the hydroxy ester (XV) has not been isolated.

*Zinc dust was used in the original experiments, but since submission of the manuscript zinc filings, amalgamated zinc, and zinc-copper couple have been employed in these laboratories by Mr. R. D. Gilbert with similar results.

In an experiment in which ethyl bromomalonate was added to a previously warmed suspension of zinc in excess cyclohexanone, no other solvent being employed, a yellow oil boiling at 240 to 250° C. (15 mm.) was obtained. This soon solidified and crystallized from hexane in colourless prisms melting at 73 to 75°. It was undoubtedly ethanetetracarboxylic ethyl ester for which Conrad and Bischoff (6) report a melting point of 76°. Found: C, 52.3; H, 7.36%. Calc. for $C_{14}H_{22}O_4$: C, 52.8; H, 6.92%.

A blank reaction without cyclohexanone was carried out between zinc and ethyl bromomalonate in boiling benzene. The zinc slowly dissolved and a viscous red liquid was formed. This was apparently a complex between the zinc and the ester, as suggested in the theoretical discussion. On burning, an inorganic residue remained, showing the presence of zinc. On acidification of this complex, ethyl malonate was produced. This complex apparently did not react with cyclohexanone, even though the latter was present in considerable excess.

When a Reformatsky reaction was attempted with cyclohexanone and ethyl bromosuccinate, ethyl succinate boiling at 125 to 127° C. (32 mm.) was obtained. This was analysed and also characterized as succinamide, m.p. 240°. In addition a reddish oil boiling at 140 to 170° (25 mm.) was isolated but this has not been identified.

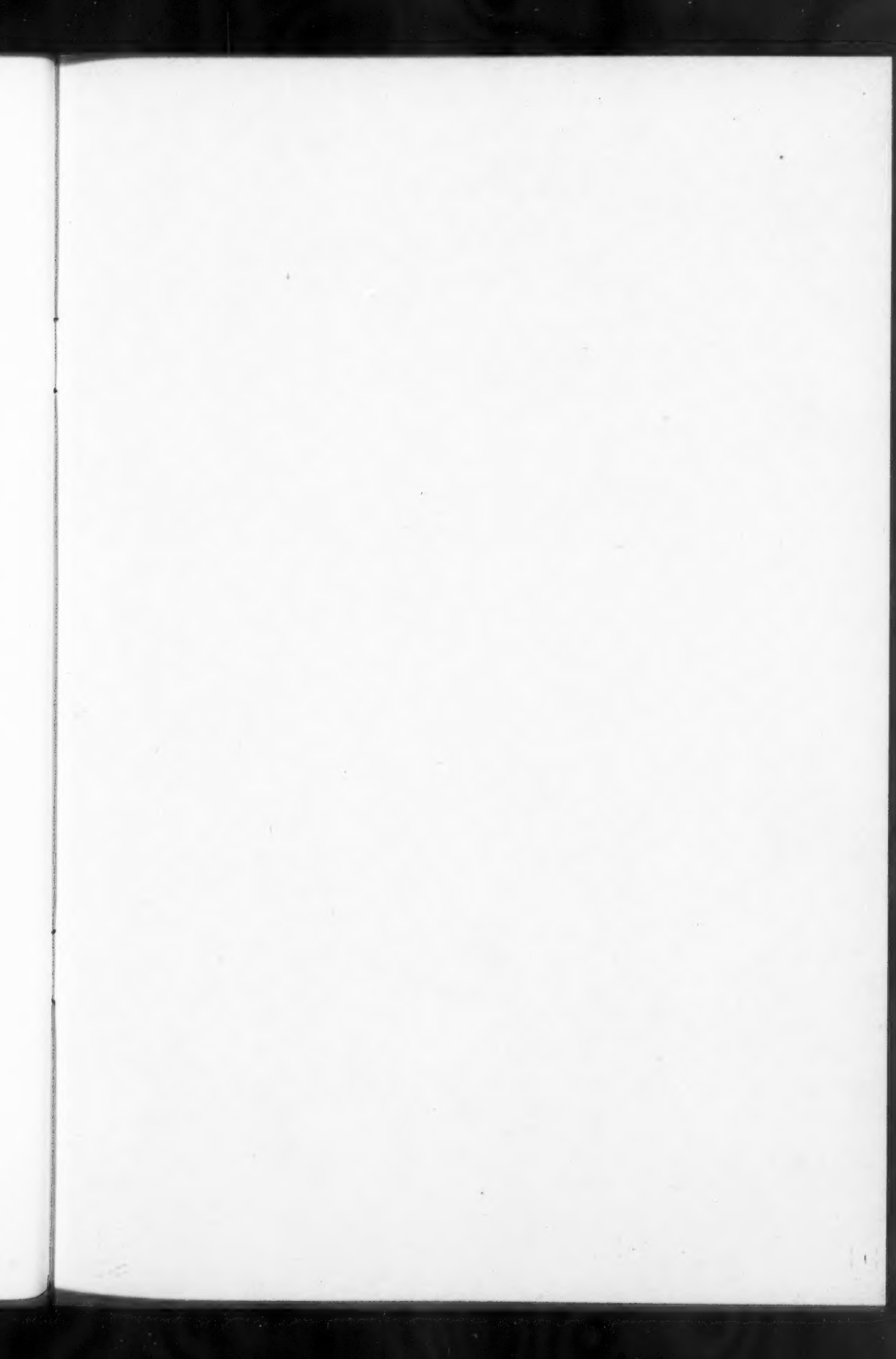
Attempted Grignard Reaction with Cyclohexanone and Ethyl Bromomalonate

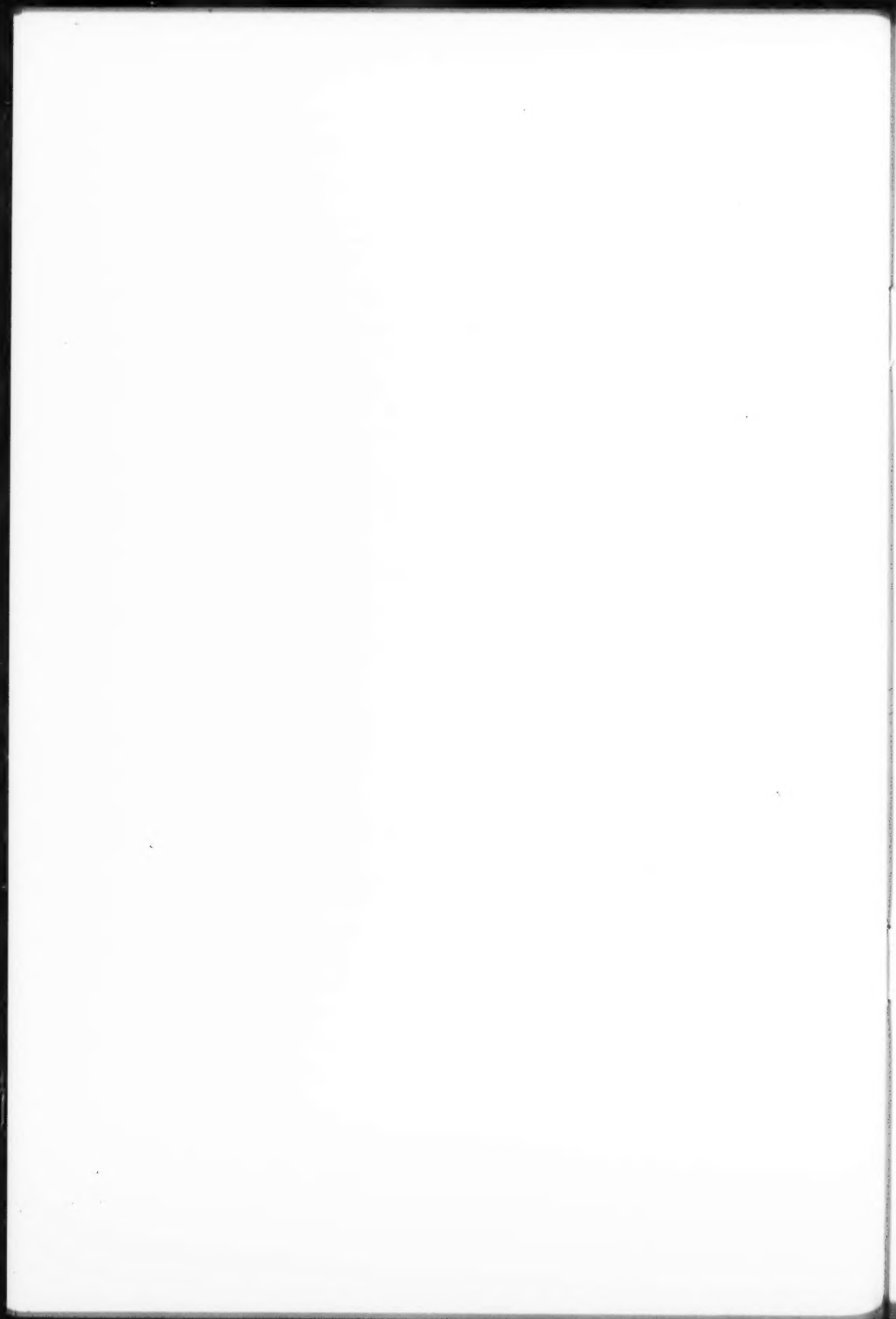
To the Grignard reagent from ethyl bromomalonate (48 gm.) and magnesium (4.9 gm.), cyclohexanone (19.2 gm.) in dry ether was added and the mixture refluxed for 1.5 hr. On working up in the usual way a yellow oil, boiling at 245 to 255° C. (23 mm.) and solidifying on cooling, was obtained. This was identified as ethanetetracarboxylic ethyl ester.

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